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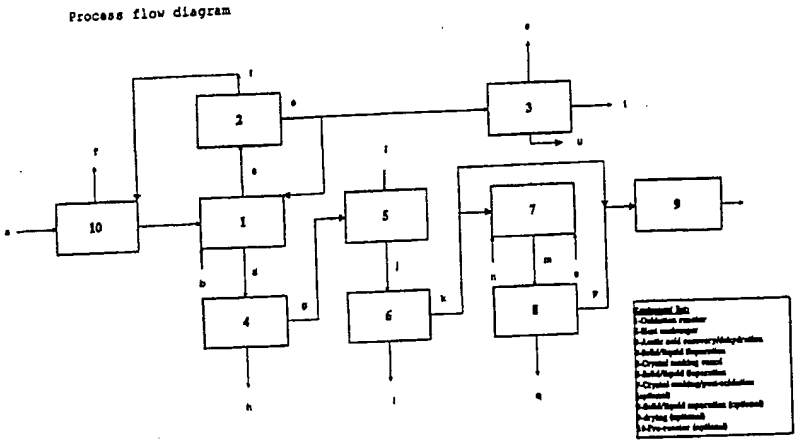

(57) Abstract

A process to produce for example terephthalic acid is provided, the process including the steps of: providing a feed stream comprising a dialkyl substituted aromatic and an organic acid solvent: contacting the feed stream with a vapour stream, the vapour stream containing at least 50 % by volume oxygen and at an oxygen partial pressure of at least 1 psi, at a temperature between about 80 °C and about 130 °C, in the presence of a catalyst system comprising zirconium and cobalt, wherein the contacting is done in a stirred tank reactor; removing from the stirred tank reactor a vapour stream comprising the organic acid and water: condensing at least a portion of the organic acid and water from the vapour stream; separating at least a portion of the water from the organic acid separated from the vapour stream; returning at least a portion of the condensed organic acid back to the stirred tank reactor; continuously recovering from the stirred tank reactor a reactor product comprising a diacid substituted aromatic; isolating solid crystals of diacid substituted aromatic from the reactor product; and recovering from the solid crystals of diacid substituted aromatic a diacid substituted aromatic having a purity of at least 97 % by weight.

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METHOD TO PRODUCE AROMATIC CARBOXYLIC ACIDS

FIELD OF THE INVENTION

The invention relates to a method to produce aromatic dicarboxylic acids.

BACKGROUND TO THE INVENTION

U.S. patent No. 3,299,125 suggests a catalyst system for production of aromatic diacids which utilizes a combination of two metals, one being cobalt, and a second being from a group which includes zirconium. This catalyst system is shown to be effective for oxidation of para-xylene to terephthalic acid at temperatures in the preferred range of 80 °C to 130 °C. This temperature range is considerably lower than that necessary using other catalyst systems. The oxidation is performed in a solvent such as acetic acid and water, and oxygen or air are bubbled through the reaction medium. At 120 °C, reaction times of 8 hours are necessary to achieve conversions of para-xylene to terephthalic acid of sixty to eighty percent. With the combination of cobalt and zirconium as the catalyst, the highest yield of terephthalic acid shown was 88%. This patent describes the advantages of the catalyst system as being the ability to eliminate halide promoters from the catalyst system, thus significantly reducing metallurgy requirements in the reactor system.

U.S. patent No. 3,700,731 suggests a cobalt-catalyzed oxidation of para-xylene wherein the reaction is performed in a continuous stirred tank reactor with hold-up times on the order of 240 minutes, with a constant withdraw of product and recycle of unreacted feed and partially oxidized intermediates. The pressure of the reaction system is such that all of the reactants are

kept in the liquid phase, and air or air enriched with oxygen up to 50% is preferred as the oxidant. The product removed from the reactor is highly impure, with terephthalic acid crystal purities of about 85%, and a large quantity of partially oxidized intermediates dissolved in the liquid phase. Terephthalic acid is removed from the reactor product by filtering crystals from a cooled reactor product, and then recycling the liquid back to the reactor. The filtered crystals are "digested" by contacting with a solvent such as acetic acid at a temperature of 200 °C to 300 °C for about ten minutes or longer, and then filtration of the digested crystals at about 100 °C and washing with hot water or acetic acid. These process operations result in a rather large recycle stream of partially oxidized intermediates to the oxidation reactor. A final terephthalic acid product is said to be 98 to 99% pure with a yield based on the starting para-xylene of 95% (molar). While the oxidation of para-xylene to terephthalic acid is highly exothermic, this patent is silent about how the oxidation reaction is cooled. Although adequate cooling of the stirred tank reactor can be achieved in a laboratory environment, it is a significant factor in design of the commercial reaction system because the produced terephthalic acid is sparingly soluble in the reaction solution. Crystals can therefore precipitate on heat exchange surfaces if temperatures of the heat exchange surfaces are significantly less than the temperature of the reaction mixture, resulting in ineffective heat removal.

The vast majority of commercially available terephthalic acid is produced by improved versions of US patent No. 2,833,816, which suggests a catalyst combination of cobalt and manganese salts and a halide promoter, for example bromine. In this system, para-

xylene is contacted with air in an acetic acid medium at temperatures in the range of 170 °C to 210 °C, and so-called "crude" terephthalic acid is produced. Over time, these systems have been improved to the point where typical crude terephthalic acid purities of 98-99.5% are produced in yields of roughly 95-96% molar based on para-xylene feed with oxidizer contact times of 45-90 minutes. However, this system suffers from significant acetic acid decomposition in the range of 5-10 lb/100 lb of terephthalic acid produced. In addition, the acetic acid and halide promoters are highly corrosive, necessitating the use of higher metallurgy, namely titanium. The contributions of acetic acid losses and titanium metallurgy significantly increase manufacturing costs.

US patent No. 5,523,474 suggests a catalyzed system with bromine promotion for para-xylene oxidation in an acetic acid medium. The reactor design is a so-called liquid oxygen reactor (LOR) which utilizes oxygen-enriched air in purities of 50-100% oxygen by volume. The benefits claimed include lower acetic acid decomposition and reduction in premature reactor shutdowns. While the patent describes the bromine-promoted system which requires titanium metallurgy, it fails to address the significant flammability concern associated with the incompatibility of oxygen-enriched air and titanium as is well known in industry and indicated in National Fire Protection Association 53 Guide on Fire Hazards in Oxygen-Enriched Atmospheres 1994 Edition.

For each of the oxidation techniques discussed above, after isolation the resulting terephthalic acid solids are generally referred to as "crude" terephthalic acid. The crude terephthalic acid can be up to 99.5% purity, with the primary impurities being 4-carboxybenzaldehyde (hereafter referred to as 4-CBA), para-toluic acid (hereafter referred to as *p*TA), and colour containing

species. Such a product is not of sufficient purity to be used directly for polyester fiber or bottle resins without additional purification, most typically by hydrogenation and re-crystallization. An example of such a purification technique is US patent No. 3,584,039.

There is also significant commercial interest in production of isophthalic acid by oxidation of meta-xylene. Isophthalic acid is typically produced by processes similar to those used for terephthalic acid.

It would be desirable to have a process to produce these dicarboxylic aromatics wherein high para-xylene yields and conversions are obtainable, wherein titanium equipment is not required, and wherein solvent oxidation is decreased. It is therefore an object of the present invention to provide an improved process for production of aromatic diacids having high yields and conversions, high crystal purities and reduced solvent decomposition losses are achieved, and reflux cooling can be utilized in a low temperature oxidation reaction system.

It is an object of a preferred embodiment of the present invention to provide an improved process for production of terephthalic acid, isophthalic acid, and mixtures of terephthalic acid and isophthalic acid.

SUMMARY OF THE INVENTION

This and other objects are achieved by a process to produce diacid substituted aromatics in a purity of at least 97%, the process comprising the steps of: providing a feed stream comprising the dialkyl substituted aromatic and an organic acid solvent; contacting the feed stream with a vapour stream, the vapour stream containing greater than 50% by volume oxygen, at an oxygen partial pressure of at least 1 psia, at a temperature between 80 °C and 130 °C, in the presence of a catalyst system comprising zirconium and cobalt, wherein the contacting is done in a stirred tank reactor; removing from the

stirred tank reactor a vapour stream comprising organic acid and water; condensing at least a portion of the organic acid and water from the vapour stream; separating at least a portion of the water from the organic acid solvent separated from the vapour stream; returning at least a portion of the separated organic acid back to the stirred tank reactor; continuously recovering from the stirred tank reactor a reactor product comprising a diacid substituted aromatic; isolating solid crystals of diacid substituted aromatic from the reactor product; and recovering the crystals of diacid substituted aromatics having a purity of at least 97% from the crystals contacted with the fresh solvent. Use of oxygen or significantly enriched air in the practice of the present invention along with reflux cooling by removing solvent vapours, and returning a portion of the condensed solvent, provides an effective partial pressure of oxygen for the oxidation reaction and avoids the presence of heat exchange surfaces in the reactor. Removal of water from the reflux provides an effective way to purge water created by the oxidation reaction.

The process also preferably includes a step wherein the isolated solid crystals of diacid substituted aromatics are contacted with fresh solvent at a temperature of between 150 °C and 250 °C for about 10 to 60 minutes. The fresh solvent is preferably water or an organic acid which does not have a significant concentration of oxidation byproducts in the solvent.

In a preferred embodiment, the alkyl substituted aromatic is para-xylene, which is oxidized to terephthalic acid and/or meta-xylene, which is oxidized to isophthalic acid.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a process flow diagram of a process for manufacturing aromatic carboxylic acids utilizing the present invention.

FIG. 2 is a graph showing calculated pressures of operation relating to example 9.

DESCRIPTION OF A PREFERRED EMBODIMENT

The method of the present invention utilizes an oxidation catalyst which has been found to be particularly effective for oxidation of aromatic alkyl groups to carboxyl groups. The catalyst system is a combination of a cobalt and a zirconium species. The cobalt and the zirconium may be in any form that is soluble in the reaction medium. Examples of such soluble forms include: organic acid salts, basic salts, complex compounds, and alcoholates. The amount of cobalt is generally between 0.01 and 1 molar in the reaction solution. The ratio of cobalt to zirconium is preferably not greater than 15:1 and more preferably between 10:1 and 5:1 molar. The catalyst can be added to the reaction mixture with the reactants or separately. The catalysts are preferably recycled from the solution of reactants by recycling the solution after the desired products have been removed by, for example, precipitation and/or filtration.

Other metals and promoters may be present in the catalyst system of the present invention, but the two metal system has been found to be effective. For example, halide promoters may be included, but it has been found that increases in activity are offset by greater metallurgy requirements. The absence of halide promoters is therefore preferred.

Referring now to FIG. 1, the species oxidized by the invention of the present invention is a dialkyl substituted aromatic provided to reactor (1). The dialkyl

substituted aromatic may be combined with the catalyst materials, or the catalyst materials could be added to the reactor separately. Para-xylene and meta-xylene are especially preferred dialkyl substituted aromatics because the resultant products are commercially valuable. Mixtures of para-xylene and meta-xylene are also commercially useful. Ethylbenzene and toluene can also be contained in unpurified xylene streams. Various oxidation intermediates of the above substituted aromatics could also be used as starting feed materials, for example para-toluic acid, para-tolualdehyde, or 4-carboxybenzaldehyde in the case of terephthalic acid being the desired product. The feeds of the present invention are provided in a solution with an organic acid solvent in stream (a). Preferable organic acids include organic acids having from two to four carbons with one carboxyl group. The most preferred solvent is acetic acid due to its vapour pressure at preferred reactor temperatures, and its solvent capabilities. These organic acids are solvents for reasonable concentrations of the feed components, the catalyst system components, and the intermediate products. The feed is preferably provided in a solution of between 5 and 25 weight percent.

The dialkyl substituted aromatic is oxidized by a vapour (b) initially containing at least 50% by volume oxygen which is added to reactor (1) in vapour (b), at an oxygen partial pressure of between 1 psia and 20 psia and preferably between 3 and 15 psia. More than 50% by volume oxygen is required so that the total pressure of the reaction system can be low enough to allow reflux cooling of the reaction system at temperatures of between 80 °C and 130 °C, and more preferably of between 110 °C and 120 °C. The reflux cooling is a result of vaporization of liquid phase components due to boiling and gas stripping, creating vent stream (c). Reflux cooling results in a

uniform reaction temperature, the only differences in temperature throughout the reactor being attributable to static head and some local differences in compositions of the solution. Further, reflux cooling eliminates cooling surfaces within the reaction vessel. It is important to eliminate cooling surfaces within the reaction vessel because the oxidized products of the present invention would tend to precipitate on the cooling surfaces and foul the surfaces. Further, the uniform temperatures of the present invention are desirable because uniform reaction temperatures reduce undesirable side reactions. The vapour stream (b) may be sparged into a liquid level in a reactor, and the noncondensable vapours in stream (c) from the reactor are either recycled or vented, but the condensable solvent and water vapours in the vent stream (c) are condensed in heat exchanger (2) for recovery. A portion of the condensed liquids may be returned to the reactor, while a portion may also be directed to a solvent recovery system (3) for removal of water from the solvent/water mixture.

The reaction of the present invention takes place in a stirred tank reactor (1) with an essentially continuous addition of reactants and withdrawal of products. Product purities increase considerably when an essentially continuous stirred tank reactor is utilized as opposed to a batch or plug flow reactor. Useful reactors may have baffles to improve contact of the sparged vapours with the liquids in the reactor, thus not being a perfect stirred tank reactor. But a significant portion of the volume is preferably subjected to significant back mixing and agitation, for example, with an impeller or jets. Because halide promoters are not necessary and the reaction is performed at relatively low temperatures, the corrosivity of the reaction medium is not particularly high. This allows use of stainless steel metallurgy as

the primary material of contact. Use of stainless steel is advantageous over titanium because of cost and safety in high oxygen concentration environments. For economic reasons, the stainless steel can be constructed as a inner cladding as the material of contact with a less expensive outer layer of carbon steel. The reactor design must also effectively provide for nearly complete oxygen consumption below the liquid/gas interface. Nitrogen can be injected in the vicinity of the liquid/gas interface in a quantity rendering the vapour phase gas mixture non-flammable. If desired, after dilution with nitrogen the unconsumed oxygen (f) can be contacted with the feed streams in optional pre-reactor (10) to provide nearly or fully complete oxygen utilization.

The oxidation of the alkyl aromatic with the oxygen stream results in production of reaction water. This reaction water may be accumulated in the system to a concentration less than 15 weight percent and preferably between 3 and 10 weight percent. It has been found that the catalyst system of the present invention is surprisingly sensitive to the presence of water in greater amounts. Some water may also be included in the feed stream to supplement the reaction water present to control solubility of the reactants, or to control the temperature and cooling of the reactor.

The unvaporized portion of the reactor contents containing both liquid and solid are essentially continuously withdrawn as stream (d) and sent to a suitable solid/liquid separator (4), which produces solids (g) containing aromatic carboxylic acid crystals with some solvent and mother liquor (h). The solid/liquid separation device effectively isolates the solid crystals from the liquid, and can in some cases also be provided with means to wash the crystals with a suitable solvent. The temperature at which the solid/liquid separation is

performed is preferably between 30 °C and 130 °C and more preferably between 50 °C and 80 °C. Examples of acceptable wash liquids include lower carboxylic acids and aqueous solutions thereof, and water. Acetic acid is most preferred, with an aqueous content less than 15% water. Examples of suitable solid/liquid separation devices include centrifuges and pressure filters. At elevated temperatures and pressures when crystal rinsing is the main objective, the Merco Disc-Nozzle centrifuge (Dorr-Oliver, Milford, Connecticut) is a particularly preferred low cost choice as the solid/liquid separation device. After the solid crystals of the aromatic diacid have been sufficiently washed, they can be furthered exposed to an additional crystal soaking operation in continuously stirred tank (5). If desired, additional fresh solvent (i) is added. Fresh solvent may be hot water, an organic acid, or a mixture thereof, but preferably does not contain a significant amount of partially oxidized alkyl aromatics. Most preferred is a 95/5 to 90/10 (w/w) acetic acid/water mixture. The temperature at which the crystal soaking operation is performed is preferably between 150 °C and 250 °C and more preferably between 180 °C and 220 °C. The contact time for the crystal soaking step is preferably between 5 and 120 minutes and more preferably between 10 and 60 minutes. The ratio of aromatic feed to solvent is preferably between 1:1 (w/w) and 1:10 and more preferably between 1:2 and 1:5. The resulting crystals are discharged as a slurry (j). If the crystal soaking operation is performed in the presence of acetic acid, nitrogen is preferably used to provide an inert environment, thus preventing oxidative degradation of the acetic acid and discoloration of the aromatic acid crystals.

When the aromatic feed is meta-xylene, the crystal soaking operation can be performed at more mild conditions, also in a continuously stirred tank. In this embodiment of the present invention the temperature at which the crystal soaking operation may be performed is preferably between 120 °C and 220 °C and more preferably between 140 °C and 200 °C.

After the initial crystal soaking is performed on the aromatic carboxylic acid crystals, an additional solid/liquid separation operation (6) can be performed in separator (6), producing solvent (l) and crystal stream (k). The crystal stream (k) can be furthered processed in a crystal soaking/post oxidation vessel (7) and/or dryer (9), or used without further processing if desirable.

Where further processing in the crystal soaking/post oxidation vessel (7) is utilized, any rinsing liquid used in solid/liquid separation device (6) is preferably water and the solid/liquid separation device should be equipped with means for formation of a cake. In so doing, crystals can be virtually freed from solvent contamination and subsequently redispersed in an aqueous medium. Such an operation is particularly preferred in the case of isophthalic acid. The temperature at which the solid/liquid separation may be performed is preferably between 50 °C and 180 °C and more preferably between 80 °C and 130 °C. These temperature ranges have the particular advantage of preventing the re-deposition of oxidation intermediates such as meta-toluic acid and 3-CBA onto the isophthalic acid crystals.

When utilizing a continuously stirred vessel as the crystal soaking/post oxidation vessel (7), the aromatic diacid crystals can be contacted with air (n) as a means of soaking the crystals and further oxidizing oxidized intermediate impurities, in the case of isophthalic acid,

namely 3-CBA and meta-toluic acid. The temperature at which the post-oxidation/crystal soaking operation is performed is preferably between 120 °C and 220 °C and more preferably between 150 °C and 200 °C. The contact time for the post-oxidation/crystal soaking step is preferably between 5 and 120 minutes and more preferably between 10 and 60 minutes. The ratio of aromatic feed to water is preferably between 1:1 (w/w) and 1:10 and more preferably between 1:2 and 1:5 which can be adjusted by addition of water (o). Upon completion of the post-oxidation operation, the wet aromatic diacid crystals (m) are isolated by a final solid/liquid separation and rinse in separator (8), producing a wet aromatic diacid (p), recovered solvent (q), and dried in dryer (9) to produce an aromatic diacid (r), which, in the practice of the present invention, will have a purity of greater than 97% by weight. The temperature at which the solid/liquid separation may be performed is preferably between 50 °C and 180 °C and more preferably between 80 °C and 130 °C. The post-oxidation step is found to be particularly effective in production of isophthalic acid due to the relatively high solubility of each of the meta isomers in water. This high solubility lowers the required operation/soaking temperature, allowing prevention of colour body formation. No catalyst addition is required in the post-oxidation step and the resulting isophthalic acid product can be utilized directly in polyester applications without further purification.

It should be noted that such a post-oxidation operation can also be performed on terephthalic acid and blends of terephthalic acid and isophthalic acid for further reductions in impurities. Such an operation can provide a product useful for some polyester applications which require less stringent specifications on oxidation intermediates and colour bodies.

Portions of organic acid streams (e), (h), (l), and (q) can be either returned to reactor (1) or sent to solvent recovery and dehydration system (3). The solvent dehydration system (3) produces stream (s) (mainly water), stream (t) (mainly purified acetic acid), and stream (u) (mainly heavy ends residue and catalysts for recovery).

EXAMPLE 1

A 316 stainless steel reactor was operated with continuous feed addition and product removal at temperatures between about 110 °C and 130 °C with residence times of one to two hours, and a feed stream of 5 to 20 weight percent para-xylene in acetic acid with a catalyst system of zirconium acetate [ZrO*$(AcO)_2$] and cobalt acetate with cobalt concentrations of 0.05 to 0.15 molar, and a cobalt to zirconium molar ratio of 7:1. The reactor was cooled with cooling coils and air was sparged into the reactor through a subsurface diptube. Acetic acid solution containing the catalyst and para-xylene feed were delivered via a positive displacement metering pump and product was continuously removed via pulsed flow through a control valve in the bottom of the reactor. Gas feed rates were monitored with mass flow controllers. The pressure was maintained at about 240 psia. Water was added to the feed in concentrations of up to 5% by weight in some runs. The reactor was provided with an air driven gas dispersing impeller.

While the temperature was adequately controlled via cooling coils, upon inspection of the reactor internals, it was observed that dramatic fouling occurred on the cooling coils. It is inferred that such fouling would render commercial system inoperable, necessitating use of evaporative cooling for extended operation.

The product from the continuous reactor was cooled to about 50 °C, and precipitate was collected on a filter.

The precipitate was prepared for analysis by combining the precipitate with 95:5 (w/w) acetic acid/water at 110 °C for a time period of 30 minutes. The resultant crystals were analyzed and purities of terephthalic acid of up to 97% percent by weight were produced, with the most significant impurities being para-toluic acid and 4-CBA. Samples of the vent gas were regularly analyzed by gas chromatography for oxygen (O_2), carbon monoxide (CO), and carbon dioxide (CO_2). Liquid and solid products were analyzed with HPLC using a 25 cm x 4.6 mm C18 column with a water/acetonitrile/methanol gradient elution program.

Results from the experiments are reported in Table 1. Methyl group conversion is defined as:

$$\frac{\text{mol methyl group consumed}}{\text{mol methyl group charged}}$$

and was computed from vent gas analysis as follows (LPM = litres per mole):

$$\frac{(O_2 \text{ uptake from air} - O_2 \text{ used in } CO_2) \text{ LPM}}{22.4 \text{ L/mol} * 1.5 \text{ mol } O_2/\text{methyl group}} \Bigg/ \frac{\text{g xylene/min in feed}}{106.1 \text{ g/mol} * 2 \text{ methyl groups/xylene}}$$

where the GC based vent gas analysis was used to determine the oxygen, carbon monoxide, and carbon dioxide concentrations in the vent gas. The burn rate is defined as:

$$\frac{(CO + CO_2) \text{ mol in vent}}{\frac{8 \text{ mol Cox/mol xylene}}{\text{mol PX converted in feed}}}$$

where the vent gas analysis was again used to compute the carbon oxide production rate and the xylene conversion was computed from the conversion described above. All combustion products were allocated to the xylene in the feed. An alternate assumption of acetic acid burning would result in a different number differing only by the carbon content of the molecules. Overall vent gas concentrations of carbon oxides ($CO+CO_2$) were about 0.8%.

In a specific example, the reactor was operated at 120 °C and 240 psia with a catalyst concentration of 0.137 molar cobalt and a 7:1 ratio of Co/Zr. Para-xylene in the feed was 9 percent by weight. The liquid phase holdup time (residence time) in the reactor was 120 minutes. Results are shown in Table 1. For this example, the methyl group conversion was 88% and about 1.7% of the para-xylene molecules were lost in the vent gas. This corresponds to a reaction selectivity of 98.3% based on para-xylene, given the assumption of negligible acetic acid decomposition. If some acetic acid is decomposed in the reaction, the selectivity should actually be a higher value. The rinsed crystals from this example were 96.6% purity and contained 2.2% para-toluic acid and 1.1% 4-CBA. The crystals were a bright white, fine powder.

EXAMPLE 2 (comparative)

A batch oxidation was carried out in the apparatus described in Example 1 at 120 °C and 290 psia by charging the autoclave with a mixture of 13% para-xylene in acetic acid. Cobalt acetate was added at a concentration of

0.1 molar to the acetic acid with a cobalt to zirconium ratio of 7:1 (molar). The oxidation was performed by starting a mixed nitrogen/air flow and then backing out the nitrogen as the catalyst became activated. The oxidation reaction was run for about 1.5 hours after which air addition was ceased. While at 120 °C, the mother liquor was drained from the vessel through a porous frit on the bottom of the vessel. Then hot acetic acid was used to re-slurry and wash the crystals at 120 °C for about 5 minutes. After drying, the resulting terephthalic acid crystals had a purity of about 84.6% with 5.7% 4-CBA and 9.7% *p*TA. With the unsteady nature of the experiment, an accurate gas phase analysis could not be obtained.

EXAMPLE 3

An oxidation reaction was performed in the apparatus used in Example 1. The reaction pressure was lowered to 55 psia and the vessel was operated at 120 °C with a 120 minute residence time. The cobalt catalyst concentration in glacial acetic acid was 0.1 molar with a 7:1 Co/Zr ratio. With a vent oxygen concentration of 4% (v/v), an oxygen partial pressure in the dry vent gas of only 2.2 psia is obtained. As shown in Table 1, the conversion was 32.4% and the aromatic burn rate was 4.6%. Under these oxygen starved conditions, the aromatic burn rate was significantly higher and very few solids were present in the reaction product indicating that only a small fraction of the product was converted to terephthalic acid.

EXAMPLE 4

An oxidation reaction was performed as in Example 1 with a mixture of 95:5 (w/w) para-xylene/meta-xylene at 13% in glacial acetic acid. The catalyst was 0.1 molar cobalt with a Co/Zr ratio of 7:1. Temperature and pressure were again 120 °C and 240 psia with a

108 minutes holdup time. The product of this reaction were crystals of a mixture of terephthalic acid and isophthalic acid, with a diacid purity of 93.3%. The remaining composition of the crystals was comprised largely of 6.7% *p*TA and 2.0% 4-CBA and low levels of mTA and 3-CBA. As shown in Table 1, the conversion was 95.1% and the aromatic burn rate was 1.2%, indicating a xylene selectivity of 98.8%, assuming no acetic acid decomposition. The crystals were a bright white, fine powder.

EXAMPLE 5

An oxidation reaction was performed as in Example 4 with 100% meta-xylene. The unit was operated with a 115 minute holdup time at 120 °C and 240 psia. The catalyst was 0.1 molar cobalt acetate and a molar ratio of cobalt to zirconium of 7:1. As shown in Table 1, a high methyl group conversion was obtained, suggesting that the catalyst system is slightly more active with meta-xylene than para-xylene. The burn rate was 1.5%, indicating a selectivity of 98.5% based on meta-xylene. The product isophthalic acid crystals were 98.8% pure, indicating a significantly higher purity than in the case of terephthalic acid. The crystals were a bright white, fine powder.

EXAMPLE 6 (comparative)

A halide promoted oxidation was performed to compare the relative burning losses of the two types of catalyst systems. A Hastalloy C reactor was constructed similarly to the stainless steel unit described in Example 1 and was operated in a semi-batch fashion with an initial charge of acetic acid and catalyst (Co/Mn/Br). To avoid a high initial concentration of reactant, para-xylene was fed continuously to the reactor at a rate of 70 g/hr. The catalyst make up was 0.52 g of manganese acetate tetra-hydrate, 0.18 g of cobalt acetate tetrahydrate, and

0.29 g of 48% HBr solution dissolved in 280 g of acetic acid containing 17.5 g of water. The oxidation was run at 205 °C and 420 psia with the catalyst and solvent initially charged to the reactor. After the feed of para-xylene was completed, the temperature was lowered to 185 °C and the oxidation was completed with an additional 15 minutes of post-oxidation to scavenge any remaining partially oxidized species in the mother liquor and to partially age the crystals. Results in Table 1 demonstrate essentially complete conversion of the para-xylene with burning losses of 3.6%. In this case, it is known that the burning losses may be attributed to both para-xylene and acetic acid. In comparison with Examples 1, and 3-5, the losses are greater than twice the amount of losses of the present invention.

EXAMPLE 7

The manner of oxidations demonstrated in examples 1, 4, and 5 produce crystals which are amenable to further purification by exposing it to a higher temperature wash stream for a time sufficient to allow partial dissolution and re-precipitation of the crystals.

A sample of oxidation product from Example 1 was combined with acetic acid with a ratio of acetic acid to terephthalic acid of 9:1 and heated to 200 °C in a continuously stirred reactor with a blanket of N_2 for a holdup time of 30 minutes. The resulting slurry was cooled to approximately 100 °C and filtered. The starting material had a purity of 91.7% terephthalic acid, with 5.8% *p*TA and 2.9% 4-CBA. After the crystal soaking step, the crystal purity was 98.4% terephthalic acid, with 0.88% *p*TA and 0.72% 4-CBA. The crystals were a bright white, fine powder, with apparently so significant change versus the starting material.

EXAMPLE 8

A sample of oxidation product from Example 5 was combined with acetic acid with a ratio of acetic acid to isophthalic acid of 9:1 and heated to 200 °C in a continuously stirred reactor with a blanket of N_2 for a holdup time of 30 minutes. The resulting slurry was cooled to approximately 100 °C and filtered. The starting material had a purity of 98.8% isophthalic acid, with 0.92% *m*TA and 0.24% 3-CBA. After the crystal soaking step, the crystal purity was 99.98% isophthalic acid, with none detected *m*TA and 0.02% 3-CBA. The crystals were a bright white, fine powder, with no significant change versus the starting material.

EXAMPLE 9

The need to operate the main oxidizer at low pressures so that reflux cooling can be utilized is most easily demonstrated with computer simulation. An Aspen 9.3 simulation using a RSTOIC block operated adiabatically was used to model the main oxidizer. The effluent from the RSTOIC block was then adiabatically flashed to generate a vapour and liquid stream. To avoid the complication of coupling the condensed overhead product with an acetic acid dehydration column, the reflux, containing over 20% water, was simply returned to the reactor. The liquid portion from the flasher was removed as product. The vapour portion leaving the flasher was cooled and the liquid condensate was returned to the reactor. The oxidizer model was operated at 99.9% para-xylene conversion with a 3% burning loss to carbon dioxide. Air was fed so that the vent gas contained 3.5% oxygen on a dry gas basis and the feed contained 15% para-xylene and 5% water in acetic acid. Results from the simulations conducted at a series of pressures are presented in Figure 2. The results demonstrate that to keep an operable oxygen partial pressure (>1 psia oxygen

partial pressure and preferably greater than >10 psia) at temperatures lower than 130 °C, an oxygen rich feed is required to allow cooling of the reactor by boiling. The higher pressures required with air to provide the necessary oxygen partial pressure would prevent boiling of the reactor contents.

Table 1: Results from Examples

Example	Targeted Product[1]	Conversion	Burn Rate	% diacid	% toluic acid	% CBA
1	TPA	96.6	1.7	96.6	2.2	1.1
2	TPA	NA	NA	84.6	9.7	5.7
3	TPA	32.4	4.6	NA	NA	NA
4	TPA/IPA mixture	95.1	1.2	93.3	6.7	2.0
5	IPA	99.2	1.5	98.8	0.92	0.24
6	TPA	101.5	3.6	99.5	0.45	0.06
7	TPA	NA	NA	98.4	0.88	0.72
8	IPA	NA	NA	99.98	nd	0.02

[1] TPA stands for terephthalic acid, IPA stands for isophthalic acid, and nd stands for none detected. For TPA, impurities listed are 4-CBA and *p*TA. For IPA, impurities listed are 3-CBA and *m*TA.

NA = Not Analyzed.

C L A I M S

1. A method to produce an diacid substituted aromatic in a purity of at least 97%, the method comprising the steps of:

providing a feed stream comprising a dialkyl substituted aromatic and an organic acid solvent:

contacting the feed stream with a vapour stream, the vapour stream containing at least 50% by volume oxygen and at an oxygen partial pressure of at least 1 psi, at a temperature between about 80 °C and about 130 °C, in the presence of a catalyst system comprising zirconium and cobalt, wherein the contacting is done in a stirred tank reactor;

removing from the stirred tank reactor a vapour stream comprising the organic acid and water:

condensing at least a portion of the organic acid and water from the vapour stream;

separating at least a portion of the water from the organic acid separated from the vapour stream;

returning at least a portion of the condensed organic acid back to the stirred tank reactor;

continuously recovering from the stirred tank reactor a reactor product comprising a diacid substituted aromatic;

isolating solid crystals of diacid substituted aromatic from the reactor product; and

recovering from the solid crystals of diacid substituted aromatic a diacid substituted aromatic having a purity of at least 97% by weight.

2. The method of claim 1 wherein the mass ratio of cobalt to zirconium is greater than about 10.

3. The method of any one of claims 1-2, wherein the temperature of the stirred tank reactor is between 110 °C and 120 °C.

4. The method of any one of claim 1-3, wherein the diacid aromatic is a xylene.

5. The method of claim 4 wherein the xylene is para-xylene.

6. The method of any one of claims 1-5, wherein the organic acid is acetic acid.

7. The method of any one of claims 1-6, wherein the concentration of the dialkyl substituted aromatic in the organic acid is between 5 and 25 weight percent based on the total feed.

8. The method of any one of claims 1-7, wherein the feed stream further comprises between 3 and 15 percent by weight water.

9. The method of any one of claims 1-8, wherein the zirconium is in the form selected from the group consisting of organic acid salts, basic salts, complex compounds, and alcoholate.

10. The method of any one of claims 1-9, wherein the cobalt is in the form selected from the group consisting of organic acid salts, basic salts, complex compounds, and alcoholate.

11. The method of any one of claims 1-10, wherein the feed stream further comprises a recycle of partially oxidized aromatics.

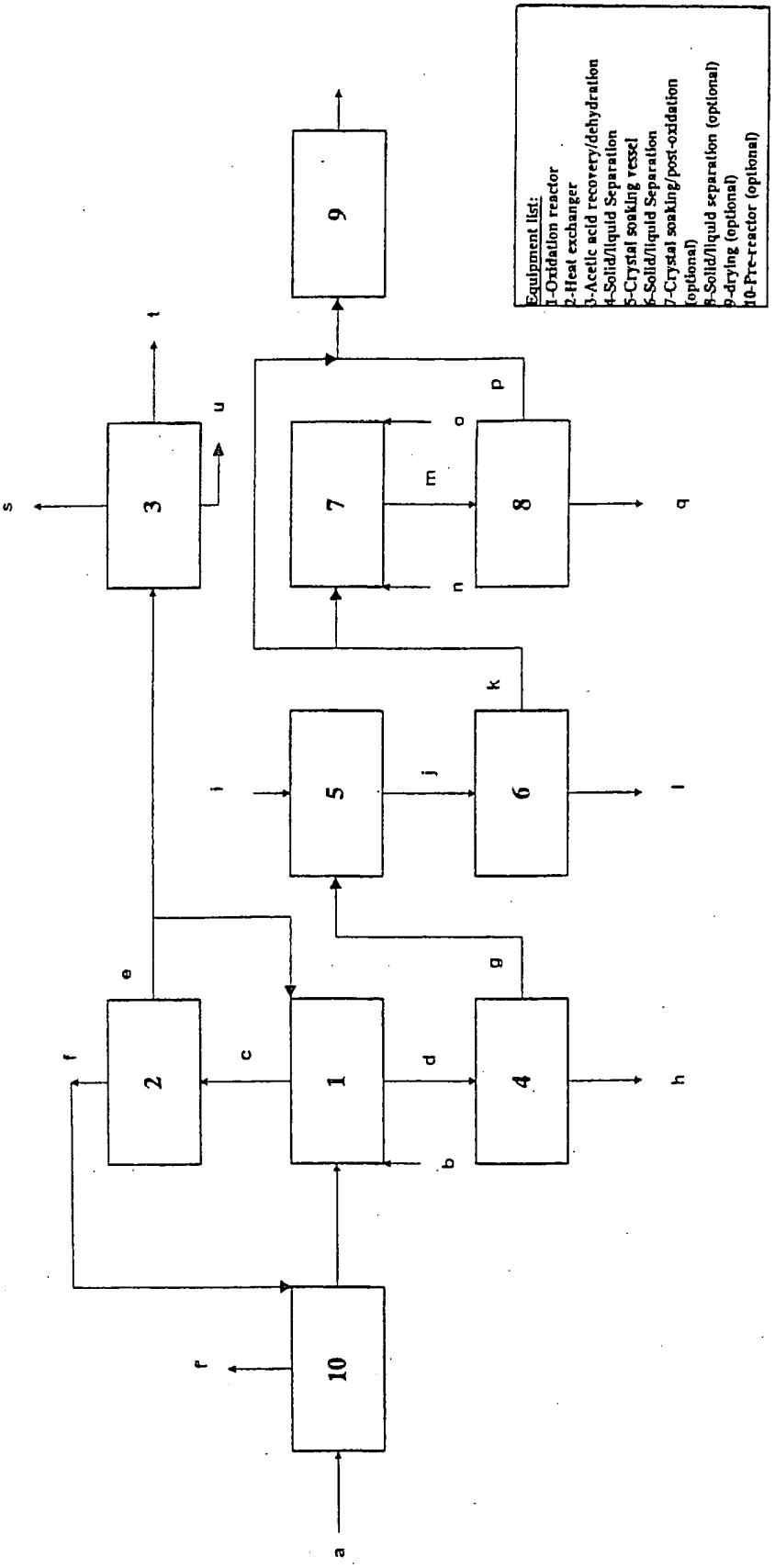
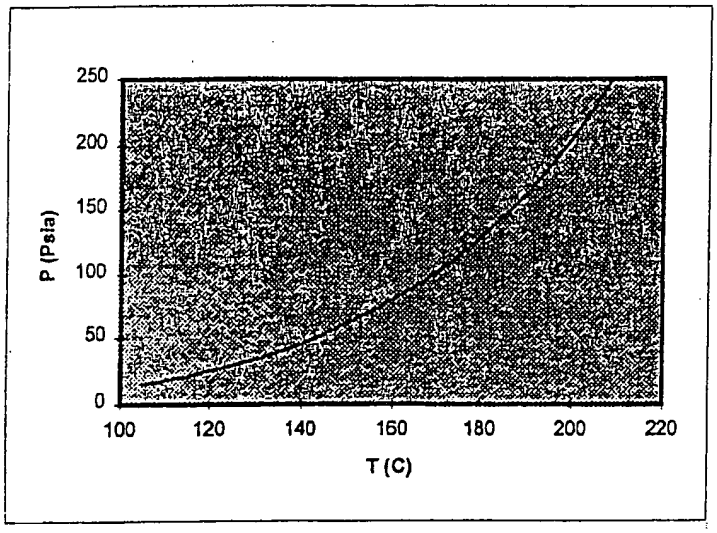


Figure 1. Process flow diagram

Figure 2: Computed pressure and temperature requires for an adiabatic boiling oxidation reactor using a 15% para-xylene feed containing 5% water in acetic acid.



INTERNATIONAL SEARCH REPORT

Inter. ional Application No
PCT/EP 98/08134

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C51/265 C07C63/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 562 318 A (BARONE BRUNO J ET AL) 9 February 1971 see claims 6,10; examples I,V,VI	1-11
Y	EP 0 754 673 A (ICI PLC) 22 January 1997 see claim 1	1-11
Y	GB 1 373 230 A (MITSUI PETROCHEMICAL IND) 6 November 1974 see page 1, line 68 - line 82; claim 1	1-11

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☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
15 April 1999	22/04/1999

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

information on patent family members

Inter ional Application No
PCT/EP 98/08134

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3562318 A	09-02-1971	BE 706159 A	07-05-1968
		DE 1668556 A	10-02-1972
		FR 1544331 A	
		GB 1215031 A	09-12-1970
		NL 6715161 A	13-05-1968
EP 0754673 A	22-01-1997	CA 2062063 A	08-09-1992
		CN 1064676 A,B	23-09-1992
		CN 1150945 A	04-06-1997
		DE 69214859 D	05-12-1996
		DE 69214859 T	27-02-1997
		EG 19876 A	30-06-1996
		EP 0502628 A	09-09-1992
		EP 0722927 A	24-07-1996
		ES 2093189 T	16-12-1996
		JP 5065246 A	19-03-1993
		MX 9200997 A	01-10-1992
		US 5563293 A	08-10-1996
		US 5527957 A	18-06-1996
		US 5679846 A	21-10-1997
		US 5877346 A	02-03-1999
		ZA 9201380 A	25-08-1993
GB 1373230 A	06-11-1974	NONE	

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